

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PBr7

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BrONO₂ + hv → products

Primary photochemical processes

Reaction		$\Delta H^\circ/\text{kJ mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
BrONO ₂ + hv → BrO + NO ₂	(1)	106	1129
→ Br + NO ₃	(2)	139	861
→ Br + NO + O ₂	(3)	155	772
→ BrONO + O(³ P)	(4)	305	392
→ Br + O(³ P) + NO ₂	(5)	347	345
→ BrO + NO + O(³ P)	(6)	412	290
→ BrONO + O(¹ D)	(7)	496	240

Absorption cross-section data

Wavelength range/nm	Reference	Comments
200-500	Burkholder, Ravishankara, and Solomon, 1995 ¹	(a)
208-500	Deters, Burrows, and Orphal, 1998 ²	(b)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\Phi_2 = 0.28 \pm 0.09$	248	Harwood, Burkholder, and Ravishankara, 1998 ³	(c)
$\Phi_2 = 1.01 \pm 0.35$	308		
$\Phi_2 = 0.92 \pm 0.43$	325.5		

Comments

- (a) Absorption spectra were measured at a resolution of ~ 0.5 nm in a 100 cm path length cell, thermostatted to ± 1 K. Relative cross-sections were obtained at 298, 250, and 220 K and placed on an absolute basis by determinations of the absolute cross-section at 330 nm at temperatures of 298 K, 273 K, 250 K, and 235 K. The concentrations of BrONO₂ were determined by pressure measurements and corrections were made to the absorption and concentration measurements for a number of impurities, particularly Br₂.

- (b) Spectra were recorded at 0.23-0.46 nm resolution using a flowing system with a multipass absorption cell of 270 cm optical path length coupled to a spectrograph and multichannel analyser. BrONO₂ concentrations were determined by photolysis of BrONO₂-Br₂ mixtures to completion, and measurement of the Br₂ concentrations by optical absorption at wavelengths >500 nm. Absorption cross-sections for BrONO₂ were obtained at 298 K and 230 K.
- (c) Excimer laser photolysis at 248 nm, 308 nm, and 325.5 nm of flowing mixtures of BrONO₂ and N₂ or O₂. [NO₃] was monitored by time resolved diode laser absorption at 661.9 nm. The laser fluence was calibrated by N₂O₅ photolysis and BrONO₂ and N₂O₅ concentrations were determined by UV absorption. The measured quantum yields were pressure independent over the range 200-790 mbar.

Preferred Values

Absorption cross-sections of BrONO₂ at 298 K and 230 K.

λ/nm	$10^{20} \sigma/\text{cm}^2$		λ/nm	$10^{20} \sigma/\text{cm}^2$	
	298 K	230 K		298 K	230 K
200	680	553	355	6.52	6.62
205	520	447	360	5.99	6.07
210	361	345	365	5.43	5.51
215	292	294	370	4.89	4.94
220	256	265	375	4.35	4.40
225	230	241	380	3.85	3.84
230	205	215	385	3.37	3.34
235	175	182	390	2.97	2.91
240	140	143	395	2.59	2.52
245	106	106	400	2.28	2.21
250	79.7	77.2	405	2.01	1.96
255	60.0	57.0	410	1.81	1.76
260	47.1	44.0	415	1.65	1.63
265	38.9	36.1	420	1.50	1.51
270	33.8	31.3	425	1.38	1.43
275	30.5	28.3	430	1.29	1.36
280	27.9	26.2	435	1.20	1.29
285	25.6	24.3	440	1.11	1.20
290	23.2	22.5	445	1.03	1.12
295	20.8	20.6	450	0.928	1.01
300	18.6	18.8	455	0.831	0.893
305	16.5	17.0	460	0.742	0.785
310	14.5	15.2	465	0.652	0.664
315	12.7	13.4	470	0.566	0.492
320	11.3	11.8	475	0.461	0.431
325	10.2	10.4	480	0.392	0.329
330	9.32	9.50	485	0.397	0.240
335	8.62	8.79	490	0.249	0.167
340	8.06	8.18	495	0.207	0.105
345	7.57	7.66	500	0.150	0.062
350	7.01	7.12			

Quantum Yields at 298 K

λ/nm	ϕ_2
248	0.28
308	1.0
325.5	0.92

Comments on Preferred Values

Our previous recommendations⁴ for the absorption cross sections were taken from the study of Spencer and Rowland⁵ which were limited to the wavelength range 186-390 nm. The more recent studies of Burkholder *et al.*¹ and Deters *et al.*² extend the range to 500 nm and cover the temperature range 220-298 K. At 298 K there is good agreement among the three studies; our preferred values are a mean of the values from Burkholder *et al.*¹ and Deters *et al.*²

There is less good agreement between the studies of Burkholder *et al.*¹ and Deters *et al.*² on the temperature dependence of the absorption coefficients. At 230 K values of σ obtained in the two studies^{1,2} agree in the range 200-300 nm but differ by up to 25 % in the range 300-500 nm, and whereas Burkholder *et al.*¹ find a small decrease in σ in going from 298 K to 230 K, over most of the wavelength range, Deters *et al.*² find an increase. The preferred values at 230 K are a mean of the values from Burkholder *et al.*¹ and Deters *et al.*²

The only quantum yield measurements are those of Harwood *et al.*,³ who determined the NO₃ quantum yield at 248, 308, and 325.5 nm, and also gave estimates of the Br and BrO quantum yields. Their values for the NO₃ quantum yields are adopted as our preferred values.

References

- ¹ J. B. Burkholder, A. R. Ravishankara, and S. Solomon, *J. Geophys. Res.* **100**, 16793 (1995).
- ² B. Deters, J. P. Burrows, and J. Orphal, *J. Geophys. Res.* **103**, 3563 (1998).
- ³ M. H. Harwood, J. B. Burkholder, *J. Phys. Chem. A* **102**, 1309 (1998).
- ⁴ IUPAC, Supplement V 1997 (see references in Introduction).
- ⁵ J. E. Spencer and F. S. Rowland, *J. Phys. Chem.* **82**, 7 (1978).